Magnetoelastic Coupling in the Spin-Dimer System TlCuCl$_3$

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We present high-resolution measurements of the thermal expansion and the magnetostriction of TlCuCl$_3$ which shows field-induced antiferromagnetic order. We find pronounced anomalies in the field and temperature dependence of different directions of the lattice signaling a large magnetoelastic coupling. The phase boundary is extremely sensitive to pressure, e.g. the transition field would change by about $\pm 185\,\%$/GPa under uniaxial pressure applied along certain directions. This drastic effect can unambiguously be traced back to changes of the intradimer coupling under uniaxial pressure. The interdimer couplings remain essentially unchanged under pressure, but strongly change when Tl is replaced by K.

One of the most simple quantum spin system is a spin-1/2 dimer. If such dimers are weakly coupled to each other, very rich and fascinating physical properties are predicted for various theoretical models and can be observed experimentally in suitable materials. For example, the two-dimensional Shastry-Sutherland model [1] is realized experimentally by SrCu$_2$(BO$_3$)$_2$ and its low-temperature magnetization as a function of magnetic field shows distinct plateaus at certain fractional values of the saturation magnetization [2]. Magnetization plateaus are also observed in the three-dimensional spin-dimer system NH$_4$CuCl$_3$ [3]. Such plateaus are, however, absent in its iso-structural (at 300 K) counterparts RCuCl$_3$ with R = Tl and K, which both have a non-magnetic ground state up to a certain magnetic field [4]. Above this field a Néel order with staggered magnetization perpendicular to the applied field occurs [5, 6] and it has been proposed that this transition should be viewed as a Bose-Einstein condensation (BEC) of magnons [7, 8, 9, 10]. According to a recent neutron scattering study, the different behavior of NH$_4$CuCl$_3$ is connected with two structural phase transitions in that compound [11]. Despite their qualitative similarity, the magnetic systems of TlCuCl$_3$ and KCuCl$_3$ show pronounced quantitative differences. The triplet excitations of TlCuCl$_3$ are strongly dispersive, whereas those of KCuCl$_3$ have a weak dispersion [10, 12, 13]. Consequently, the minimum gap $\Delta \simeq 8$ K is significantly smaller than the intradimer coupling $J \simeq 64$ K for TlCuCl$_3$, whereas this difference is much weaker for KCuCl$_3$ ($\Delta \simeq 30$ K and $J \simeq 50$ K) [10, 12, 13]. The very different behavior of the RCuCl$_3$ series shows that small structural differences strongly influence the magnetic subsystem. Evidence for a strong magnetoelastic coupling in TlCuCl$_3$ is also found in ultrasound and NMR data, which indicate that the phase transition of TlCuCl$_3$ has a significant contribution of first-order character [14, 15]. A BEC is expected to be of second order, but spin-phonon coupling can drive a continuous transition into a first-order phase transition [16]. Moreover,

hydrostatic pressure of less than 0.5 GPa is already sufficient to close Δ and to induce antiferromagnetic order in TlCuCl$_3$ without magnetic field [17, 18]. A microscopic understanding of the relevant changes under pressure is still missing. In particular, it is not clear why external pressure decreases Δ, whereas the substitution of the Tl$^+$ ions by the smaller K$^+$ ions increases Δ.

We present high-resolution measurements of the thermal expansion and the magnetostriction of a single crystal of TlCuCl$_3$. Using a capacitance dilatometer we studied the length changes perpendicular to the (010) and (10$\bar{2}$) cleavage planes of the monoclinic crystal structure [5]. Via thermodynamic relations we derive the uniaxial pressure dependencies of the transition temperatures T_c, of the transition fields H_c, of the spin gap Δ, and of the magnetic coupling constants. For Δ we find huge pressure dependencies of about $\pm 185\,\%$/GPa for uniaxial pressure perpendicular to the (010) or (10$\bar{2}$) planes, respectively. The uniaxial pressure dependencies of Δ unambiguously correlate with changes of the intradimer coupling J under pressure. In contrast to recent assumptions [10], pressure-dependent changes of the interdimer coupling J' play a minor role. Thus, the weaker J' of KCuCl$_3$ is not a consequence of chemical pressure. This gives clear evidence that the Tl$^+$ and K$^+$ ions are directly involved in the superexchange which is responsible for the relevant interdimer coupling and experimentally confirms the theoretical result of a significantly stronger superexchange via Tl$^+$ than via K$^+$ for RCuCl$_3$ [19].

In Fig. 1 we show the longitudinal thermal expansion α_i along different directions i for various values of a magnetic field applied parallel to the respective measurement directions. In low fields there are no anomalies of α_i, whereas above 6 T strong anomalies of opposite signs appear for both directions. With increasing field the anomalies increase and systematically shift to higher temperature. These anomalies signal spontaneous distortions below the phase transition: a spontaneous elongation perpendicular to the (010) and a spontaneous con-
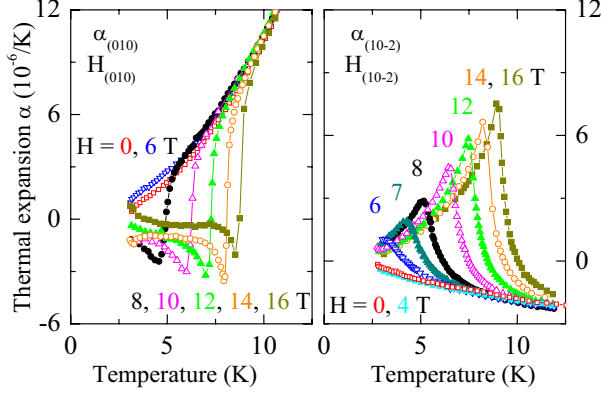
FIG. 1: Thermal expansion α_i perpendicular to the (010) and (10$\overline{2}$) planes for different magnetic-field strengths applied parallel to the respective measurement direction.

FIG. 2: Magnetostriction $\epsilon_i = \Delta L_i / L_i$ perpendicular to the (010) and the (10$\overline{2}$) planes at selected temperatures. Panel (a) shows $\epsilon_i \, vs. \, H$ and (b) $\epsilon_i \, vs. \, H^2$, respectively. Panel (c) displays the field-derivatives $\frac{\partial \epsilon_i}{\partial H}$ for $i = (010)$ obtained with increasing (line) and decreasing (symbols) field at $T = 3.8$ K.

traction perpendicular to the (10$\overline{2}$) plane.

Fig. 2 displays representative magnetostriction measurements at different constant temperatures for both measurement directions. The relative length changes $\epsilon_i = \Delta L_i(H)/L_i$ as a function of field for $i = (010)$ and (10$\overline{2}$) are again of comparable size but of opposite sign. The phase transition causes a sharp kink in ϵ_i as a function of field. With increasing temperature these kinks shift to higher fields and cannot be observed anymore in the studied field range above about 9 K. For $H > H_c$, ϵ_i changes essentially linear with field, whereas for smaller fields or for higher temperatures ϵ_i is proportional to H^2 (see Fig. 2b). A kink in ϵ_i is typical for a second-order phase transition, which should give rise to a jump-like anomaly in the field-derivative $\partial \epsilon_i / \partial H$. As mentioned above, there is some indication for a first-order contribution to the phase transition in TlCuCl$_3$. A small region of coexisting phases around H_c as proposed from the NMR data [15] can be neither confirmed nor ruled out by our measurements of the macroscopic length changes. We can, however, exclude that there is a significant hysteresis of about 0.5 T between the H_c values obtained with increasing and decreasing magnetic field as has been observed in an ultrasound study [14]. In Fig. 2c we compare $\partial \epsilon_i / \partial H$ obtained with increasing and decreasing magnetic field. As expected for a second-order phase transition there is a (broadened) jump at H_c and both curves agree well with each other over the entire field range. Thus, any hysteresis of H_c is restricted to less than our field resolution of about 50 mT.

In Fig. 3 we show the phase diagram obtained from our data (circles) together with a power-law fit (solid line) of the form $(g/2)[H_c(T) - H_c(0)] \propto T^\Phi$. This fit yields $\Phi = 2.6$ and $H_c(0) = 5.6$ T. The exponent is larger than the value of 2.1 obtained in Ref. [20] (for $T < 4$ K), but agrees well with the result of Quantum Monte Carlo (QMC) simulations [21]. According to a more recent QMC study [22], Φ sensitively depends
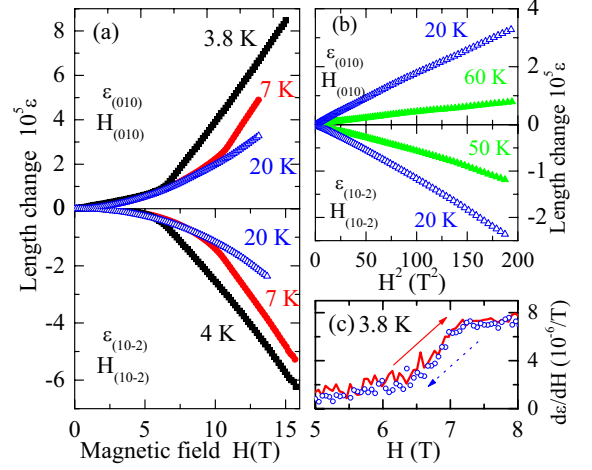
on the temperature range of the fit and in the low-temperature limit $\Phi = 1.5$ is approached, which agrees to the expected value for a BEC. Thus, our larger value of Φ arises most probably from the used temperature range $(3 \, \mathrm{K} < T < 9 \, \mathrm{K})$, but one should also keep in mind that Φ could change due to the finite spin-phonon coupling, which is not considered in the models [7, 8, 21, 22].

The anomalies at the phase boundary allow to derive the uniaxial pressure dependencies of T_c and H_c by the Ehrenfest relations

$$\frac{\partial T_c}{\partial p_i} = V_m \, T_c \, \frac{\Delta \alpha_i}{\Delta C_p} \quad \text{and} \quad \frac{\partial H_c}{\partial p_i} = V_m \frac{\Delta \frac{\partial \epsilon_i}{\partial H}}{\Delta \frac{\partial M_{mol}}{\partial H}} . \quad (1)$$

Here, V_m is the molar volume, $\Delta \alpha_i$ is the height of the thermal-expansion anomaly (see Fig. 1) and ΔC_p that of the corresponding specific-heat anomaly [20], $\Delta \frac{\partial \epsilon_i}{\partial H}$ is the slope change of ϵ_i at H_c (see Fig. 2) and $\Delta \frac{\partial M_{mol}}{\partial H}$ the corresponding slope change of the magnetization [4].

With C_p and M from Refs. [4, 20] we find huge uniaxial pressure dependencies of T_c and H_c, e.g. $\frac{\partial T_c}{\partial p_{010}} \simeq -9$ K/GPa for $T_c = 7.2$ K and $H = 12$ T, or $\frac{\partial H_c}{\partial p_{10\overline{2}}} \simeq -8$ T/GPa for $H_c = 6$ T and $T = 4$ K. A hypothetical uniaxial pressure of 0.1 GPa on (010) would strongly shift the phase boundary towards higher H_c and lower T_c values, respectively, whereas uniaxial pressure on (10$\overline{2}$) would cause a shift in the opposite direction as shown in Fig. 3 by the upward and downward triangles, respectively. The dashed and dotted lines represent power-law fits (keeping Φ fixed) of these hypothetical phase boundaries under uniaxial pressure, and their extrapolations to $T = 0$ K reveal the uniaxial pressure dependencies of Δ

$$\frac{\partial \ln \Delta}{\partial p_{10\overline{2}}} = -180 \frac{\%}{\mathrm{GPa}} \quad \text{and} \quad \frac{\partial \ln \Delta}{\partial p_{010}} = +190 \frac{\%}{\mathrm{GPa}} .$$
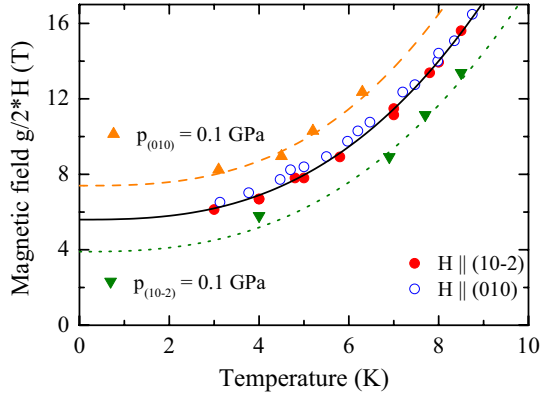
FIG. 3: Phase diagram of TlCuCl$_3$ from the magnetostriction and thermal expansion measurements perpendicular to the (010) (∘) and (10$\overline{2}$) (•) planes normalized by the respective g factors [20]. The triangles display the hypothetical shift of selected T_c and H_c values for a uniaxial pressure of 0.1 GPa perpendicular to (010) (▲) and (10$\overline{2}$) (▼) calculated by Eq. 1. The lines are power-law fits of the phase boundaries.

FIG. 4: Magnetic susceptibility (∘) with a fit for coupled dimers (solid line, Eq. 2). The dashed and dotted lines show the expected changes of χ for an increase of J and a decrease of J', respectively. Both cases would cause an increase of the spin gap Δ (see text.).

These are huge values, but due to the opposite signs, they almost cancel each other under hydrostatic pressure. Nevertheless, a strong decrease of Δ has been observed under hydrostatic pressure [17, 18]. Thus Δ should also strongly decrease for uniaxial pressure along the [201] direction, which is perpendicular to both directions of our measurements. The geometry of our crystal did not allow measurements along the [201] direction, but we expect that there will be similar anomalies at the phase boundary as those perpendicular to the (10$\overline{2}$) plane.

In a model of dimers coupled by an effective interdimer coupling J' the magnitude of Δ is determined by the balance of J and J' [10]. An increase of J will enlarge Δ, whereas an increase of J' will enhance the bandwidth of the triplet excitations and therefore lower Δ. Due to the small value of Δ compared to J (and J') in TlCuCl$_3$ already moderate pressure-dependent changes of J (or J') may cause drastic changes of Δ. In order to gain information whether these changes arise from a pressure-dependence of J or of J', we fit the magnetic susceptibility χ [23] for temperatures well above the gap by

$$\chi_{MF}(T) = \frac{\chi_0(T)}{1 + \chi_0(T) J' k_B/N_A g^2 \mu_B^2} \quad \text{with} \quad (2)$$

$$\chi_0(T) = \frac{N_A g^2 \mu_B^2 S(S+1)}{3 k_B T} \frac{2(S+1)\exp(-J/T)}{1 + 2(S+1)\exp(-J/T)} . (3)$$

Here, $\chi_0(T)$ is the susceptibility of non-interacting spin dimers with intradimer coupling J, and χ_{MF} accounts for a mean-field correction with an effective interdimer coupling J'. As shown by the solid line in Fig. 4 the fit for $T > 25$ K yields a good description of the experimental data for $J = 60$ K, $J' = 53$ K, and $g = 1.48$. Our value of J is close to the neutron scattering result $J \simeq 64$ K [8, 10, 12, 13], whereas our J' is significantly
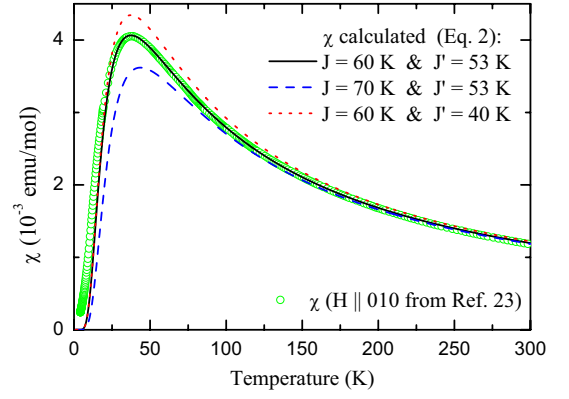
larger than the largest interdimer coupling (37 K) and our g factor is significantly smaller than $g_{010} = 2.06$ obtained by ESR [20]. One has to expect quantitative discrepancies due to our oversimplified model. However, this does hardly affect the following analysis of the relative variations around the maximum of $\chi(T)$ arising from pressure-dependent changes of J or J', because the main result is obtained from the signs of the uniaxial pressure dependencies of χ and Δ, respectively.

Let us discuss the case that Δ increases as it would under uniaxial pressure on (010). This may result either from an increase of J or from a decrease of J'. For both cases $\chi(T)$ can be modeled by Eq. 2. As shown in Fig. 4 the maximum χ_{max} *decreases* if J increases (dashed line) whereas χ_{max} *increases* if J' decreases (dotted line). Thus, the sign of the uniaxial pressure dependence of χ_{max} allows an unambiguous decision whether the uniaxial pressure dependence of Δ results from a change of J or of J'. Measurements of χ under uniaxial pressure do not exist. However, the uniaxial pressure dependence of χ is related to the magnetostriction by a Maxwell relation, and $\epsilon_i \propto H^2$ is expected for a paramagnetic material with $M = \chi H$, i.e.

$$\frac{\partial \epsilon_i}{\partial H} = -\frac{\partial M}{\partial p_i} \quad \text{and} \quad \epsilon_i = -\frac{1}{2}\frac{\partial \chi}{\partial p_i}H^2 . \quad (4)$$

As shown in Fig. 2c, the relation $\epsilon_i \propto H^2$ is indeed fulfilled and for the discussed case one finds $\epsilon_{010} > 0$ (upper panel), which implies $\partial \chi_{max}/\partial p_{010} < 0$. A decreasing χ_{max} means that the intradimer coupling J increases (see Fig. 4). The same argumentation with inverted signs for all the uniaxial pressure dependencies is valid for pressure on (10$\overline{2}$). Thus, J is the relevant parameter which changes under pressure!

The anisotropy of $\frac{\partial \chi_{max}}{\partial p_i}$ for $i = $ (010) and (10$\overline{2}$) agrees well with that of $\frac{\partial \Delta}{\partial p_i}$. This indicates that J' hardly

changes under pressure [24]. Setting $\frac{\partial J'}{\partial p_i} = 0$, our model yields $\frac{\partial \ln \chi_{max}}{\partial p_i} \simeq -0.7 \frac{\partial \ln J}{\partial p_i}$ and allows us to estimate

$$\frac{\partial \ln J}{\partial p_{10\overline{2}}} \simeq -34 \frac{\%}{\text{GPa}} \quad \text{and} \quad \frac{\partial \ln J}{\partial p_{010}} \simeq +39 \frac{\%}{\text{GPa}} \ .$$

The relative changes of J are much smaller than those of Δ, but because Δ is much smaller than J, the absolute changes of J and Δ are not too different ($\pm 22\,\text{K/GPa}$ and $\pm 14\,\text{K/GPa}$, respectively). This can be interpreted as follows. The pressure-induced change of J causes mainly a shift of the center of mass of the triplet excitations, but hardly changes its bandwidth. This is completely different from what is observed when Tl is substituted by K: The triplet excitations of $KCuCl_3$ have a much smaller bandwidth than those of $TlCuCl_3$. Our analysis of the pressure dependencies clearly shows that this smaller bandwidth is not a consequence of chemical pressure, although K^+ is significantly smaller than Tl^+. Thus the very different values of J' in $KCuCl_3$ and $TlCuCl_3$ mean that the K^+ and Tl^+ ions directly influence the effective interdimer coupling. This conclusion has been proposed also from a bandstructure calculation [19] and is now experimentally confirmed by our data. The smaller J' arises most probably from a weaker overlap via the small [Ar] shell of K^+ than via Tl^+ with the configuration $[Xe]4f^{14}5d^{10}6s^2$.

Although it is, in general, difficult to predict the microscopic changes under (uniaxial) pressure, one may understand qualitatively the uniaxial pressure dependencies of J in a simple microscopic picture. The dimers are formed by the Cu^{2+} spins of two neighboring $CuCl_6$ octahedra, which are connected via a common edge of their basal planes. The Cu–Cl–Cu bond angle amounts to $\simeq 96°$. Thus the weak antiferromagnetic coupling of $TlCuCl_3$ agrees with the expectation of the Goodenough-Kanamori-Anderson rules that the coupling changes from weakly ferro- to strongly antiferromagnetic when the Cu–Cl–Cu bond angle increases from $90°$ to $180°$. Since the line connecting the two Cl^- ions and the [010] direction have an angle of about $29°$, one may expect that pressure along [010] will shorten the Cl–Cl distance. This would increase the Cu–Cl–Cu bond angle and enhance J. The opposite may be expected for pressure along [201], since this direction has an angle of about $25°$ with the connection of the Cu^{2+} ions, and a shortening of the Cu–Cu distance would lower the Cu–Cl–Cu bond angle and decrease J. The normal of the $(10\overline{2})$ plane is nearly perpendicular to both, the Cu–Cu ($\simeq 82°$) and the Cl–Cl line ($\simeq 77°$). Thus one may expect that pressure on the $(10\overline{2})$ plane will hardly change the Cu–Cl–Cu bond angle, but will slightly increase both the Cu–Cu and the Cl–Cl distance. Therefore the Cu–Cl distances will increase and J decreases, since the overlap between the Cu-3d and Cl-2p orbitals becomes weaker.

In summary, we have presented high-resolution mea-surements of thermal expansion and magnetostriction perpendicular to the (010) and $(10\overline{2})$ planes of $TlCuCl_3$. For both directions the field-induced Néel order causes very pronounced anomalies, which allow a detailed determination of the phase boundary. There is essentially no hysteresis as expected for a second-order phase transition. The anomalies signal huge uniaxial pressure dependencies of the phase boundary, e.g. $\pm 185\,\%/\text{GPa}$ for the spin gap obtained from $H_c(0\,\text{K})$ with the signs depending on the direction of pressure. Large uniaxial pressure dependencies of opposite signs are also present for the susceptibility around $40\,\text{K}$. Our analysis unambiguously reveals that the huge pressure dependencies of Δ arise from pressure-dependent changes of the intradimer coupling, whereas changes of the interdimer coupling play a minor role. Thus, the smaller interdimer coupling in $KCuCl_3$ compared to $TlCuCl_3$ is clearly not a consequence of chemical pressure.

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[23] K. Takatsu *et al.*. J. Phys. Soc. Japan **66**(6), 1611 (1997).
[24] Since χ_{max} and Δ depend on two parameters J and J', the anisotropies of $\frac{\partial \chi_{max}}{\partial p_i}$ and of $\frac{\partial \Delta}{\partial p_i}$ will be identical in two cases: (i) if pressure changes only one parameter (in our case J) or (ii) if the anisotropies of $\frac{\partial J}{\partial p_i}$ and of $\frac{\partial J'}{\partial p_i}$ are identical. Since the second case would be accidental, it appears very unlikely.